

Rocky Flats Environmental Technology Site

Actinide Migration Evaluation

Meetings: April 29-30, 1999

Advisory Group: Greg Choppin, David Clark, David Janecky, Kirk Nordstrom

Summary and Recommendations for Path Forward

903 Pad. An impressive amount of borehole studies had been completed on and around the 903 pad, lip, and hillside areas. The wetland areas remain to be measured. The purpose of the investigation was to accurately determine the limits of tier 1 and tier 2 radionuclide levels on and around the 903 pad area. Previously, the area of investigation had all been categorized as tier 1 ($Am = 215 \text{ pCi/g}$, $Pu = 1429 \text{ pCi/g}$), but after the study, the area outside the pad and lip area (with the exception of 2 data points) are now known to be tier 2. It is therefore estimated that approximately $27,300 \text{ yd}^3$ (903 pad and lip) of soil would need to be removed to meet tier 1 cleanup levels. In order to meet tier 2 levels, it is estimated that an additional $12,400 \text{ yd}^3$ over 13 acres would need to be removed. A treatability study will consider placing a cover over the area, digging up the soil, soil washing, etc.

Solar Ponds. The design of treatability studies had begun at the university of Waterloo. A brief discussion took place where we heard about nitrate reduction in a series of sawdust and iron columns. Additional information was requested, and it was agreed that analytical data on the test results should be obtained from Waterloo, and then a more detailed discussion should take place during the July meeting to adequately discuss this topic.

Air Modeling. As a follow up to previous meeting presentations, Radian personnel presented an update on air pathway analysis. The conceptual model for source characteristics, mechanisms for release to atmosphere, and deposition of airborne particles was described in depth. Two observations were made in discussions of this work: first, roads have not been a focus for air transport pathway modeling of actinide migration, in contrast to erosion modeling, and second, remediation activities are an important aspect of release mechanisms and should be emphasized in near term work to assist the site in planning and operations.

Update on LANL experiments. Dr. Mary Neu presented an update on LANL studies to determine the oxidation state of plutonium in soils at RFETS funded by the DOE Environmental Management Science Program (EMSP). Several attempts were made to examine soil samples taken from boreholes in the 903 pad in order to experimentally determine the chemical form of plutonium in soils under the 903 pad. Two samples were obtained with sufficient plutonium concentration (9000 pCi/g , and $18,400 \text{ pCi/g}$) to attempt oxidation state and structural studies using synchrotron radiation techniques. The samples were taken to Stanford Synchrotron Radiation Laboratory (SSRL) and examined using x-ray absorption near edge structure (XANES) and x-ray absorption fine structure (XAFS) spectroscopies. The LANL research team has been using these techniques for nearly seven years, and a significant database of near edge energy positions (known to be a diagnostic of oxidation state) and fourier transform moduli (revealing bond distances and number of neighboring atoms) was shown to illustrate this point. From this database, two important standards were shown, including authentic laboratory samples of plutonium dioxide (PuO_2) and the hydrous oxide, or oxyhydroxide of tetravalent plutonium. Next we were shown XANES and XAFS spectra of the samples taken from RFETS soils. By using a combination of different characteristic x-ray absorption edges (L_{II} and L_{III}), the LANL team was able to conclusively show that the 903 pad soils contain plutonium in the tetravalent (IV)

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By B. M. Hoffman 2/12/99

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oxidation state using XANES spectroscopy. For the plutonium concentrations in the 903 pad soils, the technique is limited to within 10-15% oxidation state uncertainty. However, the XAFS data showed clearly that the sample was PuO_2 , as an authentic laboratory sample was nearly undistinguishable, and showed the well-known Pu-O distance of 2.33 Å with eight oxygen atoms near neighbors in a face-centered cubic (fcc) lattice. When compared to XAFS spectra of authentic laboratory samples of Pu(IV) oxyhydroxide, it was readily apparent that the oxyhydroxide was significantly more complex, showing a large number of peaks in the Fourier Transform resulting from a large number of Pu-O and Pu-OH distances in the low-symmetry structure. This data conclusively demonstrates that the chemical form of plutonium in soils from the 903 pad is indeed plutonium dioxide. This is a significant result because scientists studying the Rocky Flats site have maintained for decades that the form of plutonium in the soils had to be PuO_2 , but there was never any definitive proof. The present study validates many of those past claims.

Update on Erosion Modeling. Results for Antelope Springs and South Interceptor Ditch (SID) data collection and modeling work was reviewed (including information from core samples from the SID). The evolution of the modeling approach to integrate the HEC-6T code with the WEPP code to handle stream flow transport processes is a valuable enhancement. This effort continues to make good progress towards providing the site with a modeling system which can be used in assessment and predictive modes. We look forward to the addition of Dr. Lane to the AMS advisory team to extend the depth of review and input provided to the site.

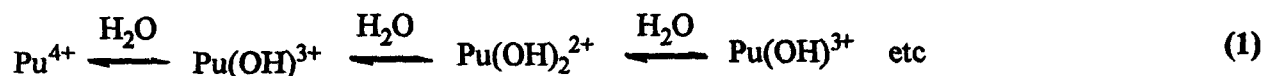
Discussion of Quarterly reports from professors Honeyman and Santchi. Collectively this work continues to address the longstanding hypothesis that reducing conditions will mobilize plutonium at the site. The quarterly reports add to the important and significant findings that reducing conditions do NOT increase the solubility of plutonium under site-specific conditions. These contributions from professors Honeyman and Santchi are extremely important, and help resolve a long-standing issue raised during the May 1995 storm event. Recent studies by Honeyman show that in fact, the solubility of plutonium decreases over time, even under reducing potentials. There are a variety of chemical consequences which can be inferred, but the overall important result remains that reducing conditions do not solubilize (and mobilize) plutonium. Professor Santchi's most recent studies aimed at oxidation state determination are still preliminary. These solvent extraction procedures are known to be complicated, and require great care and experience. The fact that Pu(V) was obtained under all conditions is an indication that the experimental details are still not satisfactorily worked out, but we are confident that a visit to the Florida State laboratories will help Santchi's team perfect the details. However, the picture that is emerging from the combined studies (including those of Dr. Neu, see "Update on LANL studies" in this report) is one in which plutonium is in the form of plutonium dioxide sorbed to particles. Honeyman and Santchi's work demonstrates that many of these particles can be quite small, in the operationally defined "colloidal size range" defined as 0.4 µm to 10 kDa. In this case, it is unlikely that solvent extraction techniques will provide useful oxidation state information for the same reasons provided in this report under the heading of "Tetra-aza Macrocycles". It is suggested that the results of solvent extraction studies be discussed in more detail at the next meeting.

Discussion of Plutonium Oxide/hydroxide. In response to questions from the regulators, Dr. David Clark from Los Alamos led a general discussion on plutonium oxide/hydroxide. The following is a summary of that discussion.

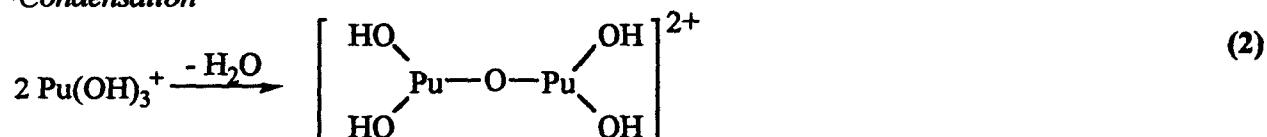
Inorganic polymers and colloids have been known since the turn of the century, and it has been known for a half a century that aqueous solutions of Pu(IV) will form colloidal polymers under the appropriate solution conditions. Early emphasis focused on avoiding Pu(IV) polymer because of its intractability and potential for interference in plutonium process chemistry. Newer concerns involve retention of plutonium in nuclear waste repositories where radioactive heating and low acidity of ground waters might favor Pu(IV) colloid formation. These so-called radiocolloids are very fine, well dispersed, intrinsic particles of radioactive compounds, whose formation in the case of the actinides is intimately connected to their hydrolysis chemistry.

Like most highly charged cations, actinide ions in aqueous solution act as acids. Protons are split off of the water molecules bound in the actinide hydration shell, and the acid strength increases markedly with the charge-to-size ratio on the central actinide ion. The simple aquo ions of the tetravalent actinides have the highest charge-to-size ratio, and are therefore the strongest acids. For metal ions in solution, the determination of the acid dissociation, or hydrolysis constants (eq 1) is of fundamental importance since their behavior in solutions as a function of pH is governed by the pK_a values. The accurate determination of pK_a values is rendered very difficult by the pronounced tendency of almost all hydroxy complexes to undergo a series of condensation and polymerization reactions as indicated qualitatively in eq 2 and 3. The oxygen atom between the two metal centers may be protonated, forming a hydroxo or oxo bridge. Two metal atoms may be bound by more than one bridge, and such polymerization eventually leads to the formation of insoluble precipitates.

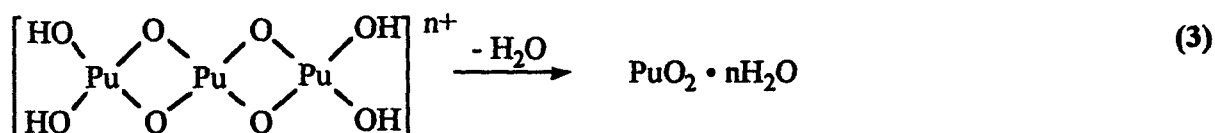
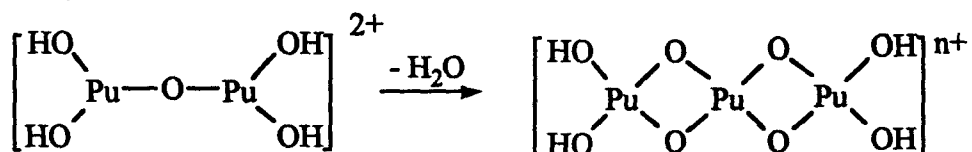
•Hydrolysis



•Condensation



•Polymerization

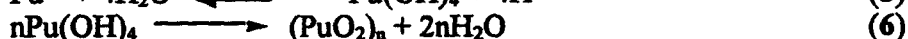
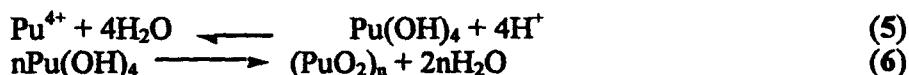


For some metal cations such as tetravalent plutonium, there is a tendency to polymerize beyond simple dimers or trimers and form extensive polymeric networks, which can reach colloidal dimensions and exists as colloidal suspensions. These species are metastable and will ultimately condense with loss of water to form oxo-bridged polymers. These polymers are

common in the d transition series, the main group, and are of particular importance in the actinide series. Ultimately, a stable metal oxide will be produced by precipitation of the hydrous polymer. This process is used industrially to generate pure oxides, and has become known as the "sol-gel" process. In the case of Si(IV) this is used extensively (eq 4)



It has long been known that solutions of aqueous Pu(IV) form these solution colloids under appropriate conditions, and this material is often referred to as "polymeric Pu(IV)". The conditions for colloid formation have been studied by many authors, and the process can be represented by eq 5 and 6



For plutonium (IV) the colloid can form solution-like sols that are optically clear, display a characteristic absorption spectrum, and do not settle on long-standing. Plutonium (IV) colloid is of particular interest in nuclear waste management because it is one of the dominant forms of plutonium under chemical conditions similar to those found in the environment. Understanding the role of colloids in the release of radionuclides and their migration in the environment is therefore of increasing importance. It was pointed out that Dr. Neu's work conclusively demonstrated that the chemical form (or speciation) of plutonium in soils under the 903 pad, were not consistent with the formation of the intrinsic colloid (or oxyhydroxide) of Pu(IV), but rather, were consistent with PuO₂ instead.

Investigation of Soil Aggregates at RFETS. Dr. Jim Ranville presented from the Colorado School of Mines provided an update on soil aggregate studies. The purpose and scope of this investigation is to determine soil properties at RFETS and how they affect erosion and transport of actinides. Dr. Ranville reviewed the importance of soil aggregation and three ways by which soil particles are cemented to form aggregates: by organic matter, by inorganic matter, chiefly iron oxides, and by physical processes such as freeze/thaw and wet/dry cycles. Aggregation is also directly linked to available surface area. The greater the aggregation the greater the surface area available for attenuating radionuclides.

Surface soil samples (both dry and runoff) have been collected from a small catchment near the SID for size distribution, for physical, chemical, and radioisotope determinations, and for disaggregation experiments. The main results reported at this meeting were the particle size distributions for the different methods of disaggregation. Five methods of disaggregation were performed to determine the main mechanism of cementation of grains: (1) deionized water - weakest method and used as a baseline for comparison, (2) ultrasonic - releases physical aggregation, (3) hexametaphosphate - releases electrostatic aggregation, (4) hydrogen peroxide - releases cementation by organic matter, and (5) citrate-dithionate-bicarbonate - releases cementation by iron and manganese oxides. Size separations included (a) sieving to >200, 53-200, and 25-53 micrometers, (b) sedimentation for 10-25 and 2-10 micrometers and (c) tangential-flow ultrafiltration for 0.45-2 micrometers, 0.45 micron-10,000 MW (molecular weight units), and <10,000 MW. Particle size analysis was also done with an optical particle counter.

Deionized water disaggregation resulted in >50% of the soil particles being >53 micrometers. This result indicates very little disaggregation. With hydrogen peroxide treatment, a distinct change occurred in the distribution with 35-45% particles of >53 micrometers and the 2-53

micrometer range making up >50% of the particles Comparing the various treatments to the deionized water treatment clearly shows

- every treatment disaggregated particles more than the water treatment
- for the <2 micrometer size range, both peroxide and sonication were the most effective at disaggregating and citrate was the least effective
- differences in properties between upper and lower parts of the watershed are not striking but do indicate an increased disaggregation from peroxide treatment

Conclusions thus far reported show that

- organic carbon plays a major role in particle aggregation,
- iron oxides play a very small role in particle aggregation
- carbonates do not appear in the top 6 inches of the soil and must be concentrated at greater depth
- Pu isotope concentrations do increase with decreasing grain size, but not as well with estimated surface area because it is a crude estimate based on grain size

Following the presentation, a discussion arose as to the nature of the radionuclide/soil particle association It is important to know what the grain size of the Pu/Am particles are with respect to the size separations Concern was expressed over the possibility of a hot particle effect in the data It was suggested that after size separations, photographic film could be used to track nuclear particles in the soil fraction It is hoped that the next set of data will have more details on radioisotope determinations and their relationship to disaggregated soil fractions

Discussion of Kd values Use and applicability of Kd values for site assessment and decision making was revisited The results of characterization of oxidation state and chemical structure from both CSM and LANL provides significant constraints on how chemical processes need to be included in models such as RESRAD

Discussion of Tetra-aza macrocycles The advisory group was provided with some viewgraphs that described recent French research on the application of tetra-aza macrocycles for selective extraction of plutonium A question was posed regarding whether this technology could be used for surface water cleanup at the RFETS site Dr Clark provided the following discussion, which was also shared during phone conversations with Bill Hayes In summary, tetra-aza macrocycles are not applicable for surface water cleanup at Rocky Flats These macrocycles, and many other novel ligands like bis triazinyl pyridine, cyanex, tri-butyl phosphate, etc, are commonly used in process chemical operations where plutonium is manipulated as a dissolved ion in solution, typically under strong acid conditions Strong acid conditions (i.e. nitric acid) are used in the process chemistry of plutonium to prohibit the hydrolysis and polymerization reactions, as discussed in this report under the heading of "plutonium oxide/hydroxide" Under these chemical conditions, ligands can be chemically tailored to show high selectivities for complexing plutonium ions over other metals ions (such as lanthanides or transition metals) However, all the data amassed to date about the chemical form of plutonium in soils at RFETS shows that the plutonium is anything but a soluble ionic form, nor is the surface water highly acidic Instead, the data indicate that plutonium is in the form of plutonium dioxide, and that it is likely attached to other mineral particles in the soils Furthermore, the data indicate that particulate (or sediment) transport is the important transport mechanism for plutonium in surface waters at RFETS Hence the novel properties of tetra-aza macrocycles, or any other molecularly-engineered ligand system are not relevant to clean-up of surface waters at RFETS

**List of Potential Peer Reviewers for
Addition to the
Actinide Migration Studies Group**

Tuesday, April 13, 1999

Following is the list of potential peer reviewers identified by the TRG members at the March 23 meeting. Each description includes the individual's degree, affiliation, and a brief summary of his/her experience.

F. Owen Hoffman, Ph.D.: Ph D in Ecology from the University of Tennessee, M S in Fisheries Limnology from Oregon State University, B A. in Biological Conservation from San Jose State College. He is currently the President and Director of SENES Oak Ridge. Professional experience includes risk analysis, environmental health physics, dose reconstruction of radionuclides and chemicals, radioecology/terrestrial/aquatic risk estimation/assessment, and statistics/quantitative uncertainty analysis.

Phillip Gschwend, Ph.D.: Ph D in Chemical Oceanography from Woods Hole Oceanographic Institution, B S in Biology from the California Institute of Technology. He is currently a Professor of Civil and Environmental Engineering at the Massachusetts Institute of Technology. Professional experience is primarily in organic chemistry, specifically organic compound contaminants in water.

Donald Langmuir, Ph.D.: Ph D, M S, and B A in Geology from Harvard University. He is currently an adjunct professor at the Colorado School of Mines and Senior Advisory Scientist at Los Alamos National Laboratory. Research interests include behavior of aqueous species, radionuclide geochemistry, metal and ligand sorption modeling and mechanics, and groundwater pollution from waste disposal.

Leonard Lane, Ph.D.: Ph D in Hydrology and Water Resources from Colorado State University, M S in Systems and Industrial Engineering and a B S in Engineering Mathematics from the University of Arizona. He currently holds a position with the Agricultural Research Service from the U S Department of Agriculture. Research interests include erosion/sedimentation, rainfall-runoff modeling, contaminant transport, infiltration, and project leader and member of core team for the Watershed Erosion Prediction Project.

Waite Osterkamp, Ph.D.: Ph D and M S in Geology/Hydrology from the University of Arizona, B A. in Chemistry and Geology from the University of Colorado. He currently holds a position with the U S Geological Survey. Professional experience includes sediment impacts, geomorphology, sediment transport, and water quality.

Donald Siegel, Ph.D.: Ph D in Hydrogeology from the University of Minnesota, M S in Geology from Penn State University, and a B S in Geology from the University of Rhode Island. He is currently a professor for Syracuse University in the Department of Earth Sciences. Publication topics include migration and dissolution of minerals, erosion effects on water quality, wetland recharge and discharge, groundwater contamination, organic complexation, and transport and attenuation of BTX.

Participants in the Actinide Migration Evaluation Meetings
April 29-30, 1999

Morning

Russel Mccallister (doe/rffo)
Tom Greengard (kh/saic)
Annette Primrose (rmrs)
Kirk Nordstrom (usgu)
Mike Peters (rmc/qa)
Win Chromec (rmrs)
Rick Roberts (rmrs)

Bob Nininger (kh)
Greg Wetherbee (wwe)
Chris Dayton (kh)
Dave Clark (lanl)
Dave Janecky (lanl)
Mary Neu (lanl)
Radian air transport workers

Afternoon

Ward Wicker
Tom Hakonson
Jerry DePorter
Brady Wilson
Laura Brooks
Elizabeth Pottorff
Jeb Love
Judy Brook
Rich Horstann

Jim Ranville
Victor Holm
Hank Stovall
John Corsi
Kathleen Meyer (rac)
Gary Kleeman (epa)
Tim Rehder (epa)
Charlie Morrison
unknown

Russel Mccallister (doe/rffo)
Tom Greengard (kh/saic)
Kirk Nordstrom (usgu)
Win Chromec (rmrs)
Greg Wetherbee (wwe)

Chris Dayton (kh)
Dave Clark (lanl)
Dave Janecky (lanl)
Mary Neu (lanl)